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Original

Removal of Mercury from Aqueous Solutions of Mercuric Chloride Using Wood Powder Carbonized at High Temperature*[1]

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Abstract——Japanese cedar (*Cryptomeria japonica* D. Don) wood powder was carbonized at varying temperatures from 400° to 2,400°C and used to remove mercury from 5 ppm mercuric chloride solutions. The removal efficiency of the carbonized wood materials changed depending on the carbonization temperature. The carbonization temperatures that provided wood powder with high removal capacity ranged from 600° to 1,400°C. Low removal of mercury from the aqueous solutions was observed for carbonization temperatures below 400° and above 1,600°C. The specific surface area of the carbonized wood materials was highly correlated with the capacity to remove mercury.

Keywords: Cryptomeria japonica, carbonization temperature, mercury, removal, specific surface area

1. Introduction

Industrialization has led to progressively higher demands for pollution-control measures. Recently, increasing attention has focused on the industrial application of charcoal especially for the adsorption of organic pollutants and heavy metals. To increase the adsorptive properties of this material, it is manufactured as activated carbon which has been extensively used in water and air purification due to its superior adsorptive properties characterized by high surface area and microporosity as well as high degree of surface activity[1–3].

Heavy metals are potential hazards in the field of environmental pollution control because of their toxicity and harmful effects. The removal of metal ions is therefore desirable to prevent these hazardous effects in the environment. Chemical precipitation, solvent extraction, ion exchance, photocatalysis etc. are some of the several methods devised to date to remove metal ions[4–6]. However, adsorption over adsorbents is still the most commonly used method for this purpose. Considering the high cost involved in preparing

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activated carbon, interest has focused on the utilization of ordinary charcoal instead of activated carbon.

In our previous studies, we used carbonized wood materials for removal of mercury from aqueous solutions of this metal. Mercury, which is toxic, quite mobile and active in biochemical metabolism, is still spreading in the environment of surface and ground water systems[7-11]. Wood powder and that carbonized at 200°, 600° and 1,000°C removed mercury within the concentration range of 1–10 ppm; mercury was preferentially removed even when mixed with other heavy metals. Wood powder carbonized at 1,000°C showed the best removal of heavy metals among the wood-based materials examined, even compared to activated carbon, in both single and mixed solutions[9]. Further, this carbonized material can remove mercury from aqueous solutions of different types of mercury compounds[10].

In this study, the removal capacity of this wood species carbonized at temperature above 1,000°C was determined using mercuric chloride as the adsorbate material.

2. Materials and Methods

2.1 Materials

The materials used were wood powder of Japanese cedar (*Cryptomeria japonica* D. Don) carbonized at 400°, 600°, 1,000°, 1,200°, 1,400°, 1,600°, 2,000° and 2,400°C. Mercuric chloride ($HgCl_2$) was used as the heavy metal compound for the removal experiments.

2.2 Carbonization process

The wood powder which was passed through a no. 20 mesh sieve, was ovendried at 105°C and then carbonized seperately at a temperature of 400°, 600°, 1,000°, 1,200°, 1,400°, 1,600°, 2,000° or 2,400°C. For 400°, 600° and 1,000°C carbonization, nitrogen (N_2) gas was passed at 100 ml/min. through the furnace and the temperature was raised at a heating rate of 4°C until the target temperature was attained. Argon gas was used for the carbonization of other materials at the same heating rate. The wood material was kept for 1 hour at the target temperature before the heater and gas flow were turned off. The carbonized wood material was taken out of the furnace after cooling overnight.

2.3 Surface area measurement

The surface area of the carbonized wood was measured using BELSORP 36. The BET (Brunaeur-Emmet-Teller) multi-point method was used to determine the surface area. Nitrogen gas at 77°K was used to determine the adsorption isotherms.

2.4 Scanning electron microscopy

The surface characteristics of raw wood powder and carbonized wood power of Japanese cedar were observed directly by scanning electron microscopy (SEM) after coating

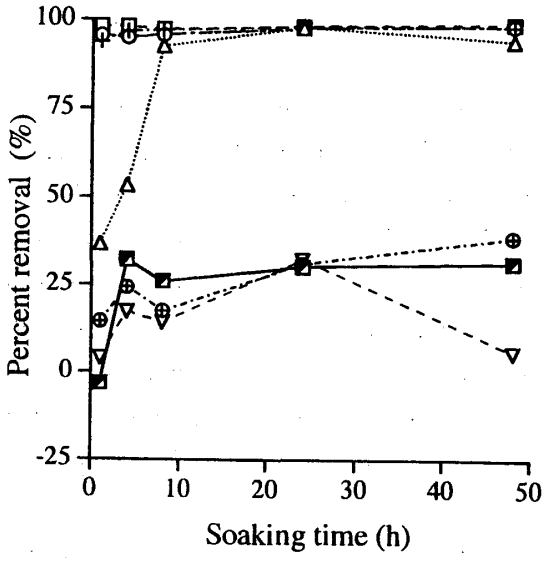

Fig. 1. Percent removal of mercury after soaking carbonized Japanese cedar wood powder in 5 ppm mercuric chloride solution. Legend: ·····△····· 400°C*, ·····□····· 1,400°C*, ---+--- 600°C*, —▣— 1,600°C*, ---○--- 1,000°C*, ---⊕--- 2,000°C*, —◇— 1,200°C*, ---▽--- 2,400°C*. Note: *-carbonization temperature.

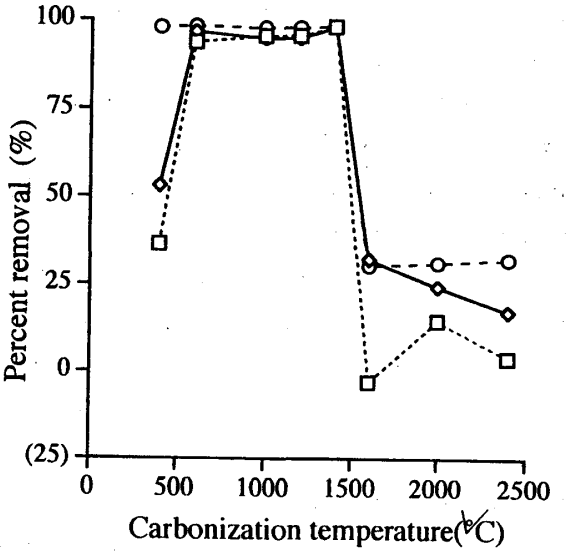

Fig. 2. Relationship between percent removal of mercury in 5 ppm mercuric chloride solution and Japanese cedar wood powder carbonized at different temperatures. Legend: ·····□····· 1 h soaking, —◇— 4 h soaking, ---○--- 24 h soaking.

with gold. Japanese cedar wood was cut into cross- and radial sections using a microtome after carbonization and examined by SEM.

2.5 Removal experiment

An aqueous solution of 5 ppm of mercuric chloride was prepared on a weight by weight (w/w) basis of mercury. Carbonized wood material (500 mg each) was added to 50 ml of the solution and continuously shaken for 1, 4, 8, 24 or 48 h in a thermostatically controlled water bath at 30°C. The mixtures were filtered and then the concentrations of mercury in the samples ware measured using an inductively coupled plasma (ICP) apparatus.

3. Results and Discussion

3.1 Effects of carbonization temperature on the removal of mercury

Fig. 1 shows the removal of mercury from 5 ppm mercuric chloride solutions using Japanese cedar carbonized wood powder. When the wood materials carbonized at 600°, 1,000°, 1,200° and 1,400°C were soaked in the solutions, mercury was removed faster than when those carbonized at 400°, 1,600°, 2,000° and 2,400°C were used. Wood powder carbonized at 600°, 1,000°, 1,200° and 1,400°C removed about 99% of the mercury after 1 h

Table 1. Yield and specific surface area of carbonized Japanese cedar wood powder

Carbonization temperature (°C)	Yield (%)	Specific surface area (m^2/g)
400	29.8	27.400
600	28.0	343.800
1,000	26.9	563.310
1,400	26.6	255.100
1,600	26.4	4.139
2,400	26.3	2.261

of soaking whereas it took about 24 h to reach almost the same level of removal using that carbonized at 400°C. The wood powder carbonized at temperatures between 1,600° and 2,400°C removed only about 25% of the mercury even after 24 h of soaking.

We demonstrated previously that that raw wood powder also removed a considerable amount of mercury at about 80% within one hour[10], but carbonization improved its capacity to remove mercury with better removal efficiency when carbonized at above 600°C. This suggested that the removal capacity of wood powder was dependent on the final carbonization temperature. As the final carbonization temperature increased, the amount of the metal removed increased. However, marked reductions in mercury removal were detected using wood materials carbonized at temperatures above 1,600°C (Fig. 2). These observations indicated that there is an optimum temperature range for carbonization of wood to remove metals from solution.

3.2 Yield and specific surface area of carbonized wood materials

Table 1 shows the yield and specific surface area of carbonized wood materials. The yield of charcoal decreased as the carbonization temperature increased. However, starting from the carbonization temperature of 1,000°C, almost the same yield was observed. Our previous report noted that specific surface area of raw wood powder without any carbonization was 0.541 m^2/g and it increased by carbonization[9]. Distinct difference in specific surface area was detected between materials carbonized at 400° and 600°C, indicating incomplete carbonization at the former temperature. Carbonization at 600°, 1,000° and 1,400°C resulted in high specific surface area, suggesting that the large amount of heat energy supplied during carbonization promoted an increase in specific surface area. On the other hand, the specific surface areas of the wood materials carbonized at 1,600° and 2,400°C were markedly reduced. The changes in specific surface area were strongly correlated with the capacity for removal of mercury from the solutions. From these results it was concluded that specific surface area of the wood materials contributed to the capacity to remove mercury from solution.

Thermal conversion of wood changes the performance properties of the product. Within a given increase in carbonization temperature, both chemical and physical

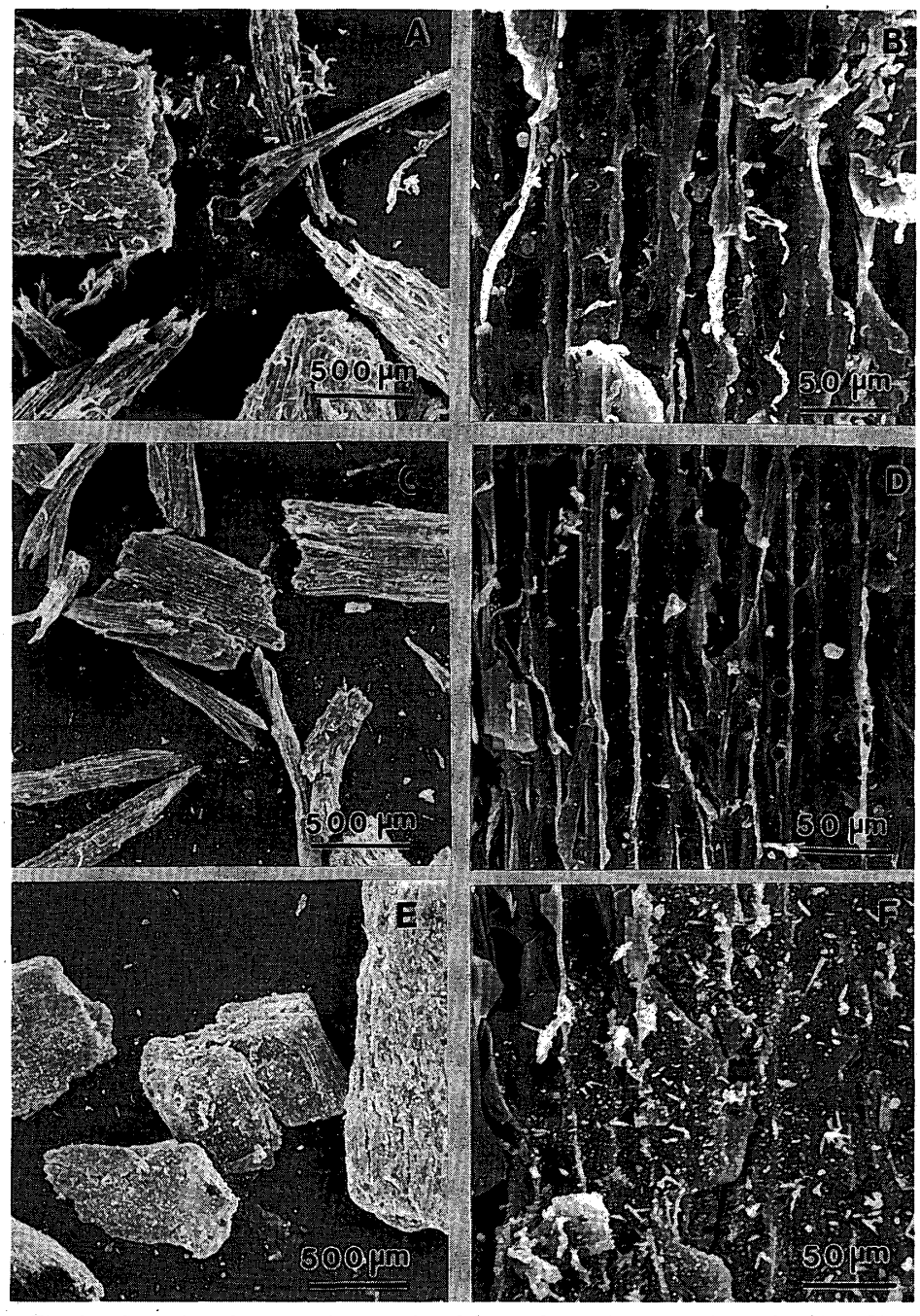

Fig. 3. Scanning electron micrographs of the surfaces of raw wood powder (A & B), and wood powder carbonized at 1,000°C (C & D) and at 2,400°C (E & F).

conversions occur. From 100° to about 3,000°C, several reactions take place affecting the performance of this material[1]. Wood begins to lose water of constitution at about 105°C and weight loss is slow up to 200°C. From 200°C to 280°C, carbon dioxide, water vapor and acetic acid are released resulting in endothermic reaction. From 280° to 500°C, rapid pyrolysis occurs and if oxygen is present the products maybe oxidized in highly exothermic

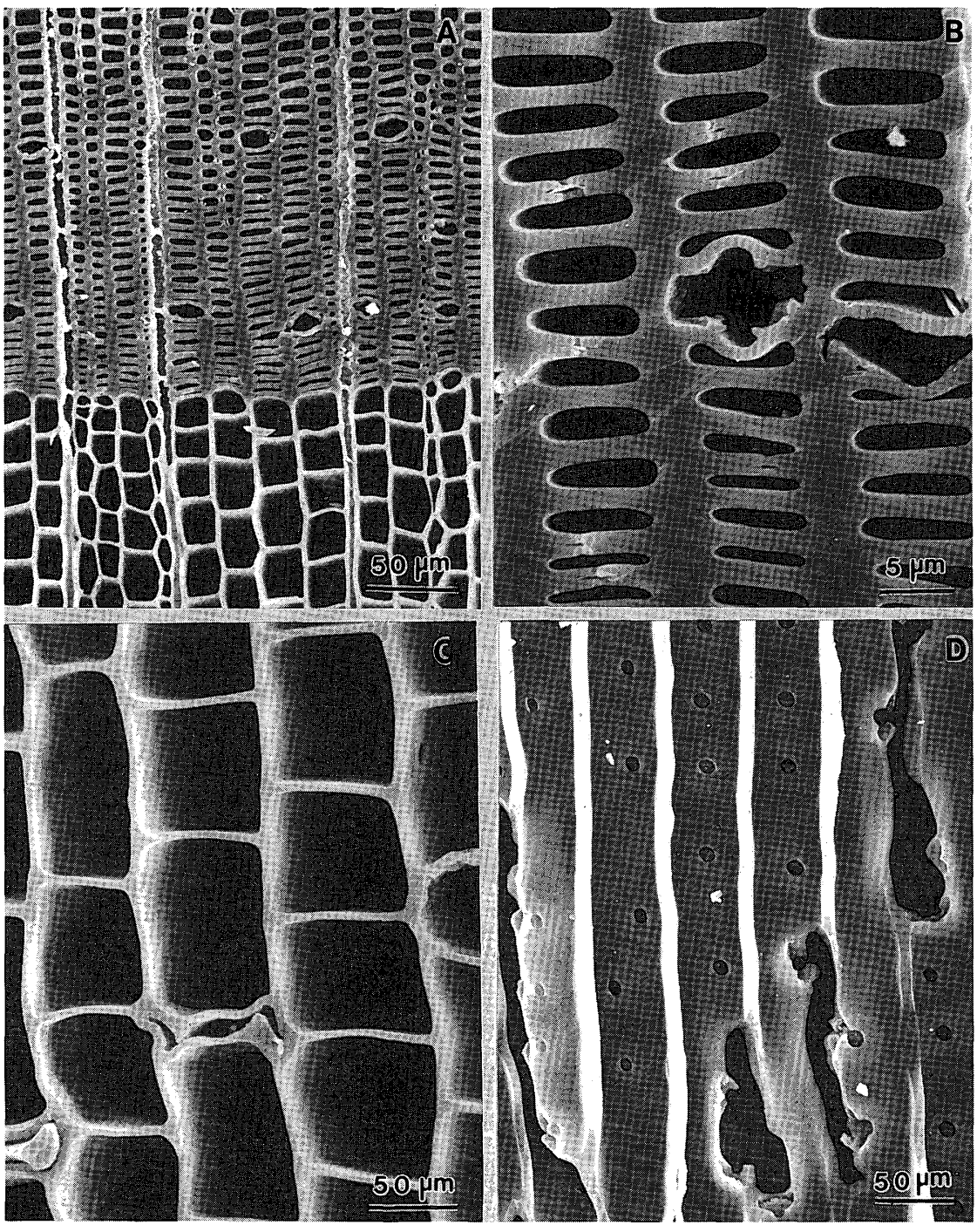

Fig. 4. Scanning electron micrographs of cross-sections (A, B, and C) and radial sections (D) of Japanese cedar wood carbonized at 1,000°C.

reactions. Combustible gases are liberated and charcoal is being formed. Carbonization is said to be completed with the temperature range of 400° to 600°C.[12,13]. Emission of these combustible gases is considered to promote the formation of micropores in the wood cells walls. As carbonization temperature was increased, the remaining volatile

substances, mainly tar, evaporated and considerable number of pores were cleared resulting in the increase of specific surface area.

On analysis of the chemical structure of wood charcoal by X-ray diffraction, peaks originating from cellulose crystalline structure disappeared when the wood was carbonized at 300°C, and no clear diffraction peaks were detected at temperatures below 1,400°C suggesting no graphitization in the charcoal[14]. In this previous report, the X-ray diffraction pattern changed gradually with increases in temperature above 1,400°C, possibly due to ultrastructural changes in the charcoal. Graphitization of wood is assumed to begin at a carbonizing temperature of about 1,800°C[1] and carbon units are suggested to be rearranged resulting in the decrease of specific surface area. The micro and ultra pores in the wood cell walls which contributed in the removal of mercury were assumed to be formed by carbonization and reformed and/or rearranged by heating.

3.3 Microstructural observations by SEM

Fig. 3 shows an over view of carbonized wood powder and enlarged view of their surface characteristics by SEM. After carbonization, the size of the wood powder became smaller and the surfaces of the samples became smooth possibly because the wood suffered from thermal degradation and decomposition. The original fibrillar arrangement of the wood structure was destroyed resulting in fragile walls within a smooth amorphous wall. After carbonization at 2,400°C, needle- or powder-like fragments were recognized adhering to the surfaces of wood powder. With sufficient heating, wood charcoal was considered to be transformed into graphite, so that the fragments were assumed to be responsible for the graphitic properties of the carbonized wood.

Cross- and radial sectional views of Japanese cedar wood carbonized at 1,000°C are shown in Fig. 4. No significant differences were observed in the cellular arrangement of earlywood and latewood or in cell wall features such as pit structures between raw wood and carbonized wood. However, glass-like fractured surfaces of cross-sections were clearly observed for the tracheid cell walls possibly due to decomposition of the cellulose fibrillar-structure.

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